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sonal equation, in that it is unmistakably influenced by previous experience. The correlations between the number of previous trials within the period and steadiness of judgment and between the number of previous periods of experience and steadiness of judgment are numerically low, but almost without exception indicate that as experience becomes greater the scatter of the individual estimates about their mean value becomes less. Probably the rate of this change is not uniform, but is most rapid at first and then falls off.

The full data and discussion are appearing in two papers in the *Psychological Review*.

POLYPEPTIDE-HYDANTOINS

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Carbon dioxide is one of the products of decomposition when certain proteins undergo hydrolysis, under normal conditions, by digestion with aqueous solutions of acids and alkalis. Mörner¹ observed the formation of this acid anhydride during an investigation of the action of hydrochloric acid (sp. gr. 1.124) on horn at 92°, but no quantitative determination of the gas was made and no special significance attributed by him to its formation. Lippich² confirmed this observation several years later and showed that this anhydride is a normal product of hydrolysis of other proteins. He also made the important observation that the quantity actually formed is dependent on the nature of the hydrolytic agent employed. Quantitative determinations of the amount of the gas evolved from several proteins under specific conditions revealed the interesting fact that the maximum quantity is obtained when an alkali, as potassium or barium hydroxide, is used as the hydrolytic agent. In no case did Lippich fail to detect the presence of this substance among his products of hydrolysis. The actual percentages obtained by hydrolysis of five different proteins with potassium hydroxide solution are recorded in Table I.

For his acid hydrolyses Lippich used 33% sulphuric acid. When these same proteins were broken down by heating with this reagent entirely different analytical results were obtained. The combinations in the proteins productive of carbon dioxide were more resistant to hydrolytic changes, under these conditions, and the maximum amount of this gas was not obtained until after 25–27 hours digestion. The percentages found are recorded in Table I.

TABLE I

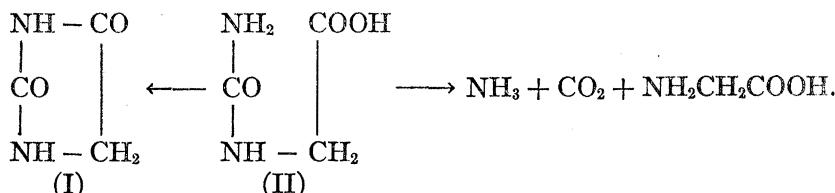
CARBON DIOXIDE

PROTEIN	<i>By acid hydrolysis per cent</i>	<i>By alkali hydrolysis per cent</i>
Parahämoglobin.....	{ 0.352 0.332 0.370 }	2.09
Egg albumin.....	0.336	2.77
Serum globulin.....	0.364	{ 2.41 2.38 }
Elastin.....	0.130	0.680
Keratin.....	0.372	{ 4.63 4.53 }

In the course of investigations now in progress in this laboratory, dealing with the study of new hydantoin and thiohydantoin combinations of biochemical interest, I had occasion to determine whether gaseous products are evolved by hydrolysis of pure fibroin and also casein. I now find that both these proteins break down on hydrolysis with sulphuric acid with evolution of carbon dioxide and obtained from casein 0.35% of its weight in the form of this gas, while three quantitative experiments with fibroin gave the values 0.20, 0.27, and 0.25% respectively. When boiling 30% barium hydroxide solution was used for the hydrolysis of fibroin (the action of barium hydroxide on casein is being investigated), we obtained the values 1.08 and 1.05% of carbon dioxide. In other words, in the cases of the two proteins elastin and fibroin about five times as much carbon dioxide is produced by alkaline hydrolysis as is obtained by digestion with sulphuric acid. By inspection of Table I it will be seen that the greatest increase was obtained by hydrolysis of keratin. The results obtained with fibroin have special significance because the production of carbon dioxide in this case does not result from the breaking down of cystin, as this protein is free from sulphur.

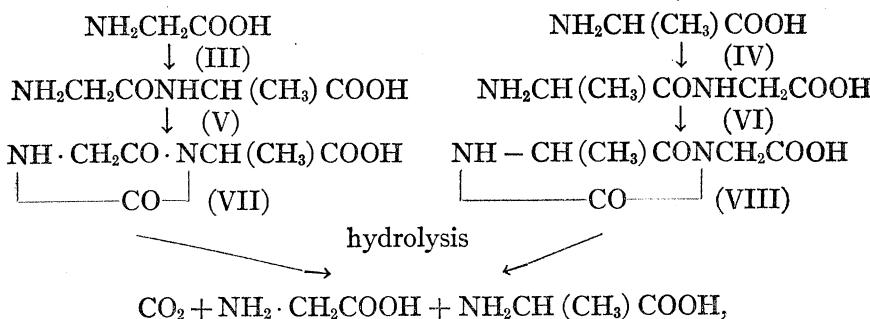
The marked difference in behavior towards acids and alkalis and the further fact that the quantity of carbon dioxide formed by hydrolysis is not proportional to the amount of arginine present in the respective proteins, suggest that urea combinations are the precursors of this gaseous hydrolytic product. Carbon dioxide would be a normal product of hydrolysis of such groupings and their destruction would be more easily accomplished by the action of alkalis than with acids. Lippich has advanced the idea that uramido acids, of which hydantoic acid II is the prototype, are the types of urea combinations which functionate in these changes. Such groupings, as is well known, are hydrolyzed by alkalis with formation of α -amino acids, carbon dioxide and ammonia.

On the other hand, when heated with acids, they easily undergo inner condensation with transformation into their corresponding anhydrides or *hydantoins* I. The latter compounds are very resistant to further hydrolysis with acids as has been shown by investigations in this laboratory.



While this explanation of Lippich's is in concordance with the chemical nature of hydantoic acids, on the other hand these compounds (II) do not represent the only types of uramido combinations which can undergo hydrolysis with formation of carbon dioxide and α -amino acids. One point needs to be taken into consideration here and that is the fact, that for every molecule of carbon dioxide formed by hydrolysis of a hydantoic acid II an equivalent amount of ammonia must also be obtained. Apparently this ratio $\text{CO}_2:\text{NH}_3$ has never been established quantitatively in the case of a single protein.

Theoretically it is possible to link together two α -amino acids in a cyclic urea combination in such a manner that the resulting compound will undergo hydrolysis with production only of carbon dioxide and α -amino acids. If we choose glycocoll III and alanine IV as the two amino acids and combine them in the form of hydantoins as represented by formulas VII and VIII, two isomeric cyclic combinations will be obtained which will fulfil the above conditions. In other words, they are cyclic derivatives of the two isomeric dipeptides—glycylalanine V and alanylglucine VI respectively, in which the characteristic polypeptide groupings of the dipeptides have been preserved. Such combinations are the representatives of a new class of hydantoins,

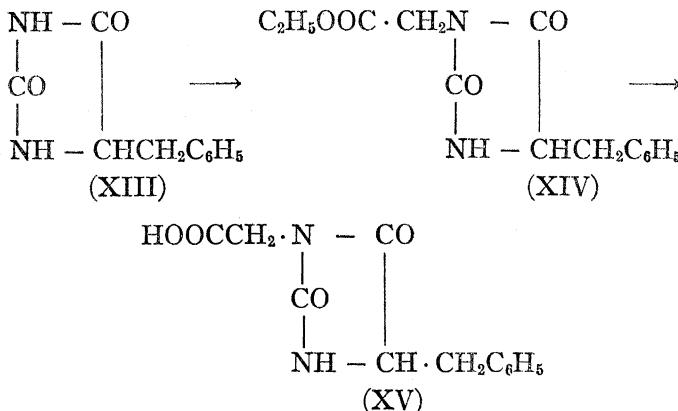


to which we have assigned the name—*polypeptide-hydantoins*. The hydantoin derivatives of the polypeptides—glycylphenylalanine **IX**, phenylalanyl glycine **X**, glycyltyrosine **XI** and tyrosineglycine **XII** are now being investigated. Their formulas are:

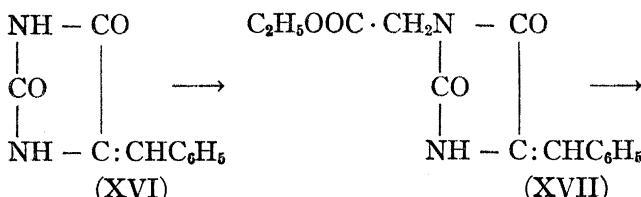
- (IX) $\text{NH}_2\text{CH}_2\text{CO} \cdot \text{NHCH}(\text{CH}_2\text{C}_6\text{H}_5)\text{COOH}$
- (X) $\text{NH}_2 \cdot \text{CH}(\text{CH}_2\text{C}_6\text{H}_5) \cdot \text{CONH} \cdot \text{CH}_2\text{COOH}$
- (XI) $\text{NH}_2 \cdot \text{CH}_2\text{CONH} \cdot \text{CH}(\text{CH}_2\text{C}_6\text{H}_4 \cdot \text{OH})\text{COOH}$
- (XII) $\text{NH}_2\text{CH}(\text{CH}_2\text{C}_6\text{H}_4\text{OH})\text{CONHCH}_2\text{COOH}$.

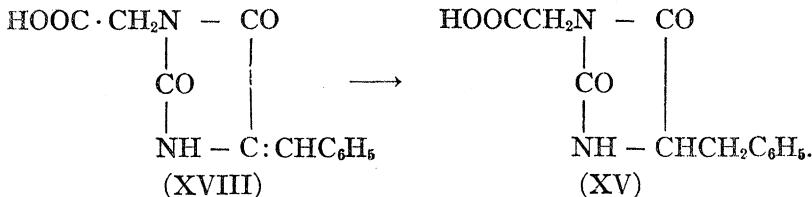
The polypeptide-hydantoin **XV** (m. 184–185°) has already been synthesized and two methods have been developed for its preparation which are apparently of general application:

(1) Alkylation of 4-benzylhydantoin³ **XIII** with ethyl chloracetate with formation of the ester **XIV** (m. 157°), which is easily converted into the *polypeptide-hydantoin* **XV** by saponification.



(2) Alkylation of 4-benzalhydantoin⁴ **XVI**, with ethyl chloracetate with formation of the ester **XVII** (m. 174°). The latter gives by saponification the unsaturated acid **XVIII** (m. 258°), which undergoes reduction smoothly giving the *polypeptide-hydantoin* **XV**.





Other methods for synthesizing hydantoin compounds of this type (and their sulphur analogues) are being developed. This work will include not only the study of hydantoin derivatives of dipeptides but also tripeptide combinations of analogous constitution, and also an investigation of their behavior towards hydrolytic agents and enzymes.

¹ Mörner, *Zs. physiol. Chem.*, **34**, 207 (1901).

² Lippich, *Ibid.*, **90**, 441 (1914).

³ Wheeler and Hoffman, *Amer. Chem. J.*, **45**, 368 (1911).

⁴ Ruhemann and Cunningham, *London, J. Chem. Soc.*, **75**, 958 (1899); Ruhemann and Stapleton, *Ibid.*, **77**, 246 (1900); Wheeler and Hoffman, *loc. cit.*

RECENT EXPLORATIONS IN THE CACTUS DESERTS OF SOUTH AMERICA

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Read before the Academy, November 16, 1915. Received January 6, 1916

When the cactus investigation for the Carnegie Institution of Washington was taken up a few years ago with Dr. N. L. Britton, a definite plan for field work in the deserts of North and South America was outlined. And since the Cactus family is confined to America, this meant a survey of its entire distribution.

The exploration of the deserts of South America was referred to me, and I have spent two seasons in exploring these regions; the first on the west coast, in Peru, Bolivia, and Chile, and the second on the east coast, in Brazil and Argentina. The exploration was confined chiefly to the deserts, as the cacti as a class are desert loving plants. A cactus desert, however, does not necessarily mean a desert like the Sahara or the desert of Arizona.

We found as a result of our investigation that South America contains six great cactus regions: (1) The desert of northern South America, including northern Venezuela and Colombia. This region we have not yet studied at first hand. (2) The great Peruvian and Chilean desert which extends from northern Peru to central Chile and from the Pacific Ocean to the top of the Andes, having a length of 2000 miles and a breadth of 50 to 300 miles. (3) The desert of Argentina, extending from the central part of Patagonia along the east side of the Andes well into Bolivia.